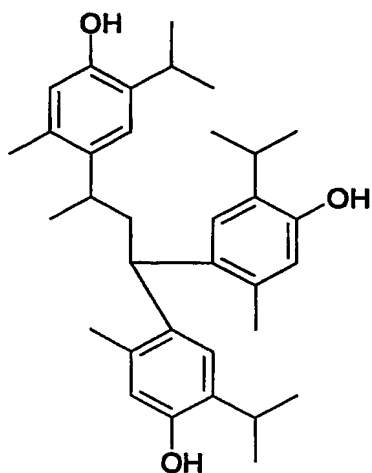


Claims

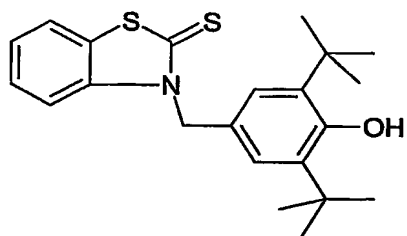
1. Method of coloring a polymeric material, wherein a polymeric material containing

- a) a phenolic antioxidant and/or a phenolic ultraviolet absorber and
- b) a colour former

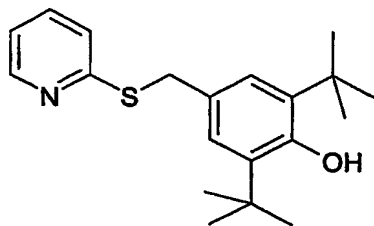
is irradiated using a radiation of higher energy than visible light, provided that the phenolic antioxidant and/or phenolic ultraviolet absorber (a) is not a compound of the formula (2) to (14)



(2)

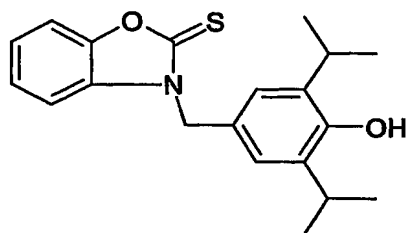


(3)

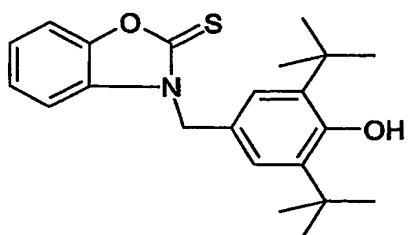


(4)

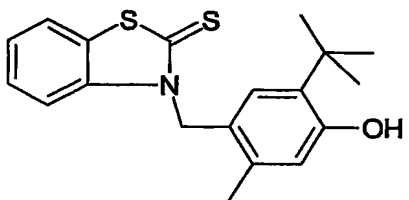
- 60 -



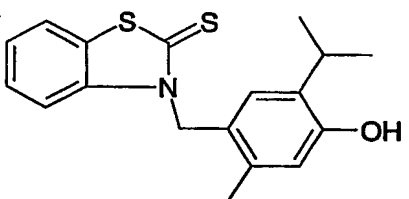
(5)



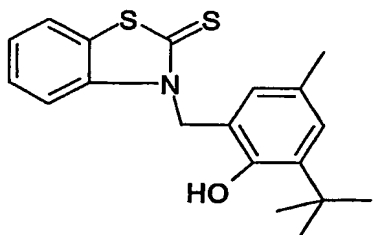
(6)



(7)

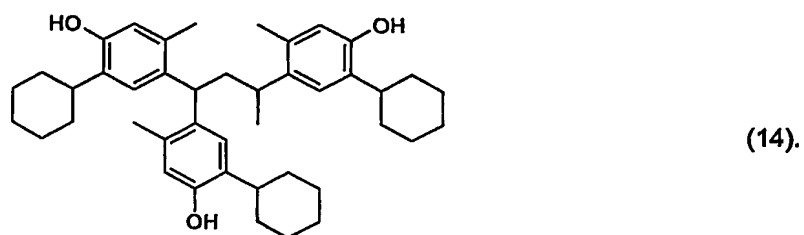
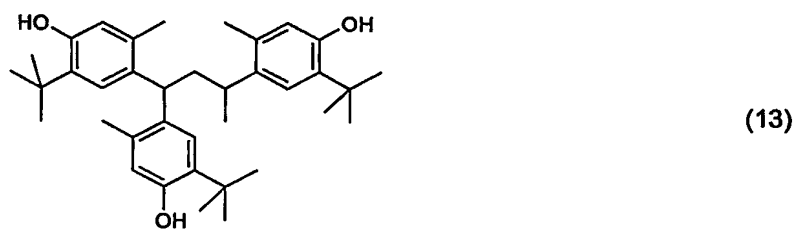
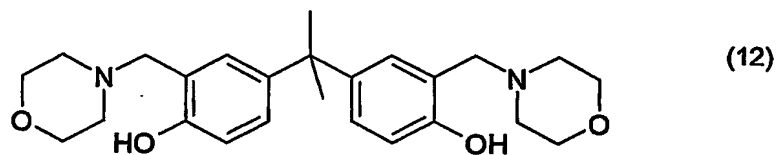
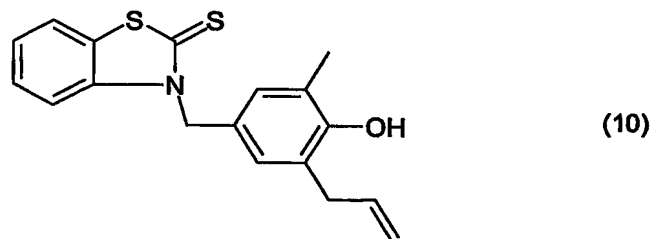


(8)



(9)

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2. Method according to claim 1, wherein the radiation of higher energy than visible light is selected from ultraviolet light, X-ray, gamma radiation and particle radiation, especially from

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ultraviolet laser or ultraviolet lamp radiation of 285 to 400 nm, electron radiation, X-ray and gamma radiation.

3. Method according to claim 1, wherein component (a) is a compound comprising one or more mono-hydroxyphenyl moieties, each carrying one or two bonds to either a linking group connecting the moiety with 1 to 3 further moieties of the same type or to an anchor group,

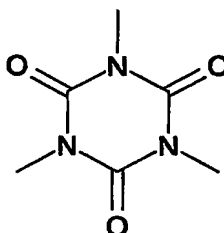
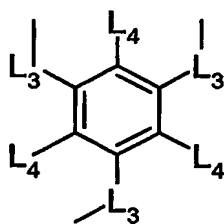
and optionally 1-3 further substituents selected from alkyl of 1 to 12 carbon atoms, where the linking groups are di-, tri- or tetravalent aliphatic groups of 1 to 20 carbon atoms and divalent linking groups are selected from

alkylene which may be interrupted and/or end-capped with $-O-$, $-NH-$, $-S-$, $-CO-$, $-COO-$, $-OCO-$, $-NHCO-$, $-CONH-$, a group L_1 , phenylene, phenylene which is substituted by C_1 - C_{12} alkyl and/or C_1 - C_{12} alkoxy and/or C_2 - C_{12} alkanoyloxy and/or C_3 - C_{12} alkenoyloxy;

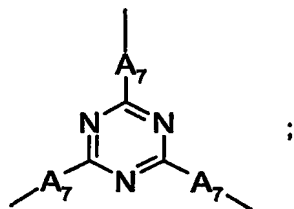
divalent mono-, di- or tricycloalkylene groups; divalent mono-, di- or tricycloalkylene groups interrupted by $-O-$; spacer groups $-O-$, $-NH-$, $-S-$, $-CO-$, $-COO-$, $-OCO-$, $-NHCO-$, $-CONH-$;

trivalent groups are selected from

trivalent alkyl groups of 3 to 20 carbon atoms; said trivalent alkyl groups interrupted and/or end-capped with $-O-$, $-NH-$, $-S-$, $-CO-$, $-COO-$, $-OCO-$, $-NHCO-$, $-CONH-$, a group L_1 , phenylene, phenylene which is substituted by C_1 - C_{12} alkyl and/or C_1 - C_{12} alkoxy and/or C_2 - C_{12} alkanoyloxy and/or C_3 - C_{12} alkenoyloxy; or trivalent groups of the formulae

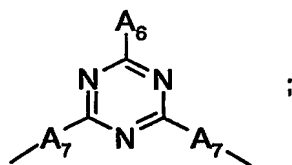
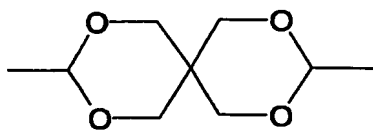
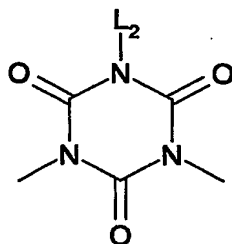


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tetravalent groups are selected from
 tetravalent alkyl groups of 4 to 20 carbon atoms; said tetravalent alkyl groups interrupted
 and/or end-capped with -O-, -NH-, -S-, -CO-, -COO-, -OCO-, -NHCO-, -CONH-, a group L₁,
 phenylene, phenylene which is substituted by C₁-C₁₂alkyl and/or C₁-C₁₂alkoxy and/or C₂-
 C₁₂alkanoyloxy and/or C₃-C₁₂alkenoyloxy;
 wherein

L₁ is a group selected from the formulae



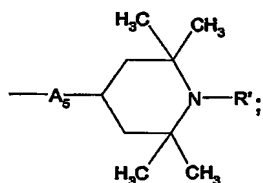
L₂ is OH, C₁-C₁₂alkyl, C₁-C₁₂alkoxy, C₂-C₁₂hydroxyalkyl; C₂-C₁₂hydroxyalkoxy;
 L₃ independently are C₁-C₄alkylene;

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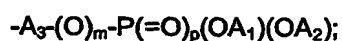
L_4 independently are H or C_1 - C_4 alkyl; and

anchor groups are selected from

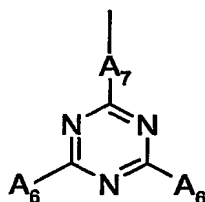
C_1 - C_{22} alkyl; C_1 - C_{22} alkyl- A_5 -; C_2 - C_{22} alkyl interrupted by $-A_5$ -; $-A_4$ -phenyl; $-A_4$ -phenyl where the phenyl core is substituted by C_1 - C_{12} alkyl, C_1 - C_{12} alkoxy, C_2 - C_{12} alkanoyloxy and/or C_3 - C_{12} alkenoyloxy; C_1 - C_8 alkyl substituted by a group of the formula



phosphite, phosphate or phosphonate ester groups, e.g. of the formula



or the anchor group is of the formula



where m and p independently are 0 or 1;

A_1 and A_2 independently are C_1 - C_{12} alkyl or phenyl or phenyl substituted by C_1 - C_{12} alkyl or an equivalent of an alkaline, alkaline earth or aluminum atom;

A_3 is a direct bond or C_1 - C_8 alkylene;

A_4 is selected from C_1 - C_8 alkylene and A_5 ;

A_5 is selected from $-O-$, $-NH-$, $-S-$, $-CO-$, $-COO-$, $-OCO-$, $-NHCO-$, $-CONH-$;

A_6 is selected from C_1 - C_{18} alkoxy, C_1 - C_{18} alkylthio and C_1 - C_{18} alkylamino;

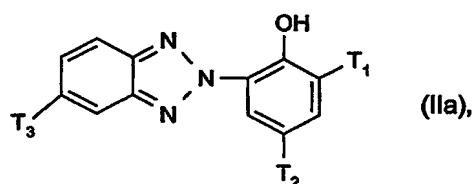
A_7 is $-O-$ or $-NH-$;

R' is H, C_1 - C_{18} alkyl, C_1 - C_{18} alkoxy or cyclohexyloxy;

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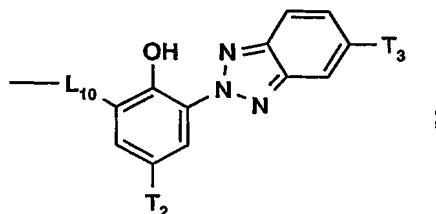
or the anchor group is C₃-C₂₂alkylene or C₃-C₂₂oxaalkylene attached with both open bonds to adjacent carbon atoms of the mono-hydroxyphenyl moiety;

component (a) can also be a phenolic UV absorber compound selected from benzotriazoles of the formula (IIa), 2-hydroxybenzophenones of the formula (IIb), 2-hydroxyphenyltriazines of formula (IIc):



wherein T₁ is hydrogen, C₁-C₁₈alkyl, or C₁-C₁₈alkyl which is substituted by phenyl,

or T₁ is a group of the formula



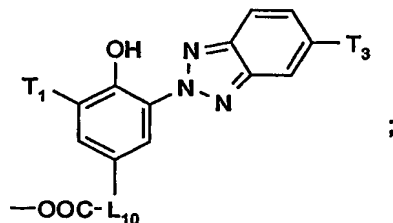
L₁₀ is a divalent group, for example -(CH₂)_n-, where n is from the range 1-8;

T₂ is hydrogen, C₁-C₁₈alkyl, or is C₁-C₁₈alkyl which is substituted by COOT₅, C₁-C₁₈alkoxy, hydroxyl, phenyl or C₂-C₁₈acyloxy;

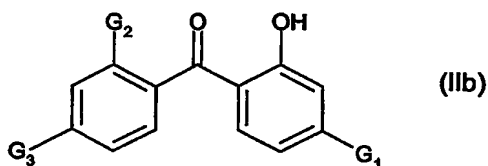
T₃ is hydrogen, halogen, C₁-C₁₈alkyl, C₁-C₁₈alkoxy, C₂-C₁₈acyloxy, perfluoroalkyl of 1 to 12 carbon atoms such as -CF₃, or T₃ is phenyl;

T₅ is C₁-C₁₈alkyl or C₄-C₅₀alkyl interrupted by one or more O and/or substituted by OH or by

a group

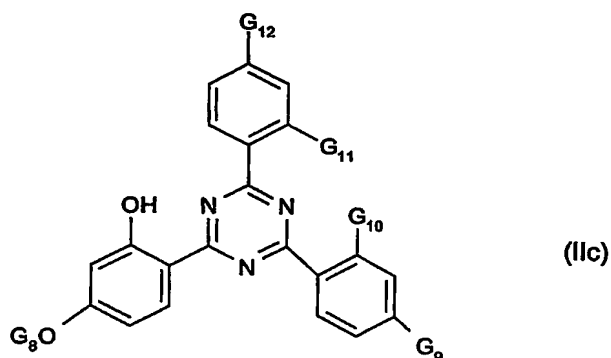


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wherein

G₁, G₂ and G₃ independently are hydrogen, hydroxy or C₁-C₁₈alkoxy;



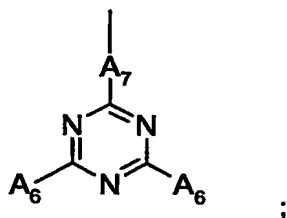
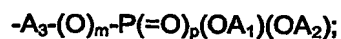
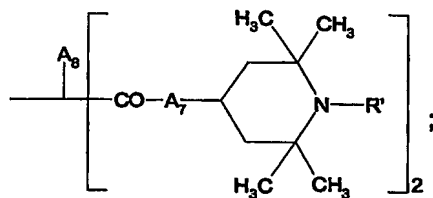
wherein

G₈ is C₁-C₁₈alkyl, or is C₄-C₁₈alkyl which is interrupted by COO or OCO or O, or is interrupted by O and substituted by OH;

G₉, G₁₀, G₁₁ and G₁₂ independently are hydrogen, methyl, hydroxy or OG₈; and G₉ and G₁₂ also comprise phenyl.

4. Method according to claim 3, wherein the anchor groups are selected from tertiary C₄-C₁₂alkyl; C₁-C₂₂alkyl-A₅-; C₂-C₂₂alkyl interrupted by -A₅-; -A₅-phenyl; -A₅-phenyl where the phenyl core is substituted by C₁-C₁₂alkyl; -A₄-phenyl where the phenyl core is substituted by C₂-C₁₂alkanoyloxy and/or C₃-C₁₂alkenoyloxy, and optionally further by C₁-C₁₂alkyl; or the anchor group is C₃-C₂₂alkylene or C₃-C₂₂oxaalkylene attached with both open bonds to adjacent carbon atoms of the mono-hydroxyphenyl moiety; or is a group of one the formulae

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where m and p independently are 0 or 1;

A₁ and A₂ independently are C₁-C₁₂alkyl or phenyl or phenyl substituted by C₁-C₁₂alkyl or an equivalent of an alkaline, alkaline earth or aluminum atom;

A₃ is a direct bond or C₁-C₈alkylene;

A₄ is selected from C₁-C₈alkylene, -O-, -NH-, -S-, -CO-, -COO-, -OCO-, -NHCO-, -CONH-;

A₅ is selected from -O-, -NH-, -S-, -CO-, -COO-, -OCO-, -NHCO-, -CONH-;

A₆ is selected from C₁-C₁₈alkoxy, C₁-C₁₈alkylthio and C₁-C₁₈alkylamino;

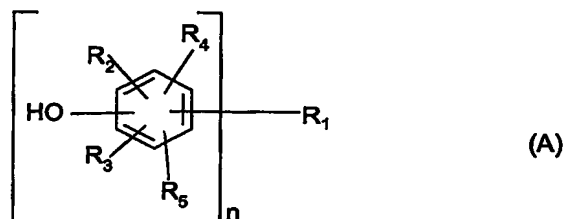
A₇ is -O- or -NH-;

A₈ is C₁-C₇alkyl;

R' is C₁-C₁₈alkyl.

5. Method according to claim 3, wherein component (a) is a compound of the formula (A)

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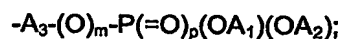
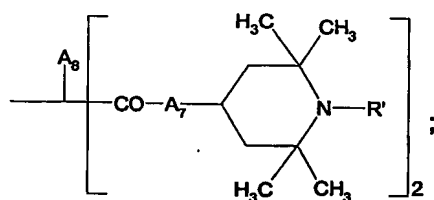
wherein

R_2 , R_3 , R_4 and R_5 independently are hydrogen, methyl or tertiary C_4 - C_{12} alkyl, especially methyl, tert.-butyl and tert.-pentyl;

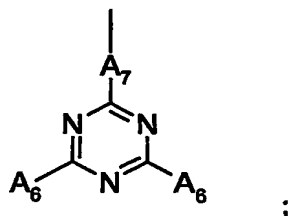
n is from the range 1-4;

when n is 1,

R_1 is tertiary C_4 - C_{12} alkyl; C_1 - C_{22} alkyl- A_5 -; C_2 - C_{22} alkyl interrupted by $-A_5$ -; $-A_5$ -phenyl; $-A_5$ -phenyl where the phenyl core is substituted by C_1 - C_{12} alkyl; $-A_4$ -phenyl where the phenyl core is substituted by C_2 - C_{12} alkanoyloxy and/or C_3 - C_{12} alkenoyloxy, and optionally further by C_1 - C_{12} alkyl; or R_1 together with R_5 is C_3 - C_{22} alkylene or C_3 - C_{22} oxaalkylene attached with both open bonds to adjacent carbon atoms of the mono-hydroxyphenyl moiety; or is a group of one the formulae



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where m and p independently are 0 or 1;

A₁ and A₂ independently are C₁-C₁₂alkyl or phenyl or phenyl substituted by C₁-C₁₂alkyl or an equivalent of an alkaline, alkaline earth or aluminum atom;

A₃ is a direct bond or C₁-C₈alkylene;

A₄ is selected from C₁-C₈alkylene, -O-, -NH-, -S-, -CO-, -COO-, -OCO-, -NHCO-, -CONH-;

A₅ is selected from -O-, -NH-, -S-, -CO-, -COO-, -OCO-, -NHCO-, -CONH-;

A₆ is selected from C₁-C₁₈alkoxy, C₁-C₁₈alkylthio and C₁-C₁₈alkylamino;

A₇ is -O- or -NH-;

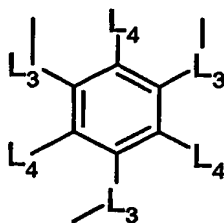
A₈ is C₁-C₇alkyl;

R' is C₁-C₁₈alkyl;

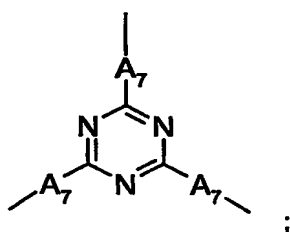
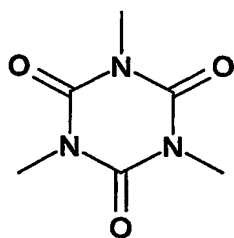
when n is 2, R₁ is C₁-C₂₀alkylene which may be interrupted and/or end-capped with -O-, -NH-, -S-, -CO-, -COO-, -OCO-, -NHCO-, -CONH-, -L₁-, phenylene, phenylene which is substituted by C₁-C₁₂alkyl and/or C₁-C₁₂alkoxy and/or C₂-C₁₂alkanoyloxy and/or C₃-C₁₂alkenoyloxy;

divalent mono-, di- or tricycloalkylene groups; divalent mono-, di- or tricycloalkylene groups interrupted by -O-; spacer groups -O-, -NH-, -S-, -CO-, -COO-, -OCO-, -NHCO-, -CONH-;

when n is 3, R₁ is trivalent alkyl of 3 to 20 carbon atoms; said trivalent alkyl interrupted or end-capped with -O-, -NH-, -S-, -CO-, -COO-, -OCO-, -NHCO-, -CONH-, -L₁-, phenylene, phenylene which is substituted by C₁-C₁₂alkyl and/or C₁-C₁₂alkoxy and/or C₂-C₁₂alkanoyloxy and/or C₃-C₁₂alkenoyloxy; or trivalent groups of the formulae

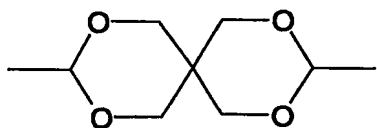
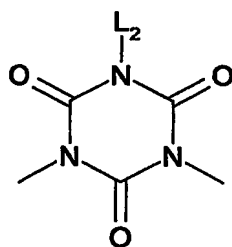


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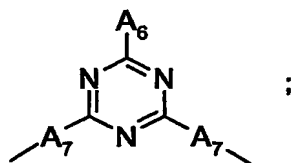


when n is 4, R_1 is tetravalent alkyl of 4 to 20 carbon atoms; said tetravalent alkyl interrupted or end-capped with $-O-$, $-NH-$, $-S-$, $-CO-$, $-COO-$, $-OCO-$, $-NHCO-$, $-CONH-$, $-L_1-$, phenylene, phenylene which is substituted by C_1 - C_{12} alkyl and/or C_1 - C_{12} alkoxy and/or C_2 - C_{12} alkanoyloxy and/or C_3 - C_{12} alkenoyloxy;

L_1 is a group selected from the formulae



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L₂ is OH, C₁-C₁₂alkyl, C₁-C₁₂alkoxy, C₂-C₁₂hydroxyalkyl; C₂-C₁₂hydroxyalkoxy;

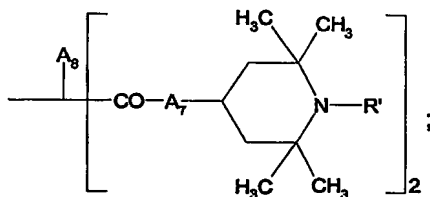
L₃ independently are C₁-C₄alkylene;

L₄ independently are H or C₁-C₄alkyl.

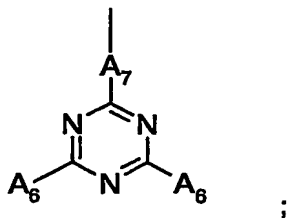
6. Method according to claim 5, wherein R₂, R₃, R₄ and R₅ independently are hydrogen, methyl, tert.-butyl, tert.-pentyl;

when n is 1,

R₁ is tertiary butyl, tertiary pentyl; C₁-C₂₂alkyl-A₅-; C₂-C₂₂alkyl interrupted by -A₅-; -A₅-phenyl where the phenyl core is substituted by C₁-C₁₂alkyl; -A₄-phenyl where the phenyl core is substituted by C₃-C₄alkenoyloxy and C₁-C₁₂alkyl; or R₁ together with R₅ is C₃-C₂₂alkylene or C₃-C₂₂oxaalkylene attached with both open bonds to adjacent carbon atoms of the mono-hydroxyphenyl moiety; or R₁ is a group of one the formulae



-A₃-P(=O)(OA₁)(OA₂);



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A₁ and A₂ independently are C₁-C₄alkyl or an equivalent of a metal atom selected from Li, Na, K, ½ Mg, ½ Ca, 1/3 Al;

A₃ is methylene;

A₄ is C₁-C₈alkylene;

A₅ is selected from -O-, -S-, -COO-, -OCO-, -NHCO-, -CONH-;

A₆ is selected from C₄-C₁₈alkylthio and C₄-C₁₈alkylamino;

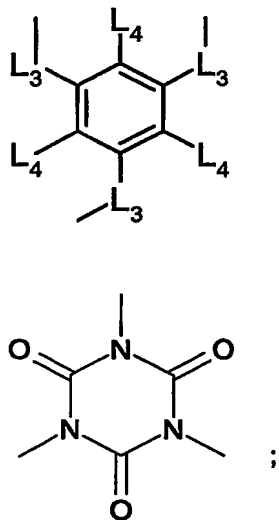
A₇ is -NH-;

A₈ is C₁-C₇alkyl;

R' is C₁-C₁₈alkyl;

when n is 2, R₁ is C₁-C₁₂alkylene; C₂-C₂₀alkylene interrupted and/or end-capped with -O-, -S-, -COO-, -OCO-, -NHCO-, -CONH-, -L₁-; or R₁ is a divalent mono-, di- or tricycloalkylene group; or R₁ is -O-, -NH-, -S-;

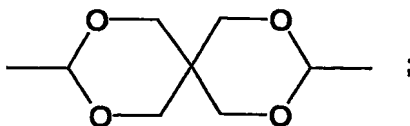
when n is 3, R₁ is trivalent alkyl of 3 to 20 carbon atoms; said trivalent alkyl interrupted by -O-, -S-, -COO-, -OCO-, -NHCO-, -CONH-, phenylene, phenylene which is substituted by C₁-C₁₂alkyl; or R₁ is a trivalent group of one of the formulae



when n is 4, R₁ is tetravalent alkyl of 4 to 20 carbon atoms; or said tetravalent alkyl interrupted by -O-, -S-, -COO-, -OCO-, -NHCO-, -CONH-;

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L₁ is a group of the formula



L₃ independently are C₁-C₄alkylene;

L₄ independently are H or C₁-C₄alkyl.

7. Method according to claim 1, wherein the colour former is a triphenylmethane, lactone, benzoxazine, spiropyran or preferably fluoran or phthalide.

8. Method according to claim 1, wherein the polymeric material contains 0.001 to 10 % by weight of the phenolic antioxidant and/or phenolic UVA, based on the total weight of the polymeric material.

9. Method according to claim 1, wherein the polymeric material contains 0.001 to 10 % by weight, preferably 0.01 to 5 % by weight of the colour former with respect to the total weight of the polymeric material.

10. Method according to claim 1, wherein the polymeric material is a transparent thermoplast.

11. Method according to claim 1, wherein the polymeric material is selected from styrene acrylonitrile copolymer, polyolefin, polyvinylchloride, polychlorobutadiene, polyesters and glycol modified polyesters, polyacrylics, polystyrene, acrylonitrile styrene acrylate copolymer, polyamide, acrylonitrile styrene butadiene copolymer, polycarbonate, or blends or alloys thereof.

12. Method of coloring a polymeric material, wherein a polymeric material containing

- c) a phenolic antioxidant, phenolic ultraviolet absorber and/or a latent acid, and
- d) a colour former

is irradiated using a radiation of higher energy than ultraviolet light.

13. Protective clothing or mask or irradiation indicating tag, wherein a polymer material comprising components (c) and (d) according to claim 12 in form of a fiber, textile, non-woven or film is contained on visibly below the surface of the clothing or tag.

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14. Process for monitoring irradiation by X-ray or radioactive material, which process comprises placing a tag or sample of a polymer material comprising components (c) and (d) according to claim 12 in the site to be controlled, and subsequently checking the colour of the tag or sample.

15. Use of a polymer material comprising components (c) and (d) according to claim 12 for detecting irradiation by X-ray or radioactive material.

16. Process of making a fiber or woven or non-woven fabric, which process comprises adding (a) a phenolic antioxidant and/or phenolic UVA and (b) a colour former to a synthetic polymer before or during the fiber melt spinning process.